Confidential

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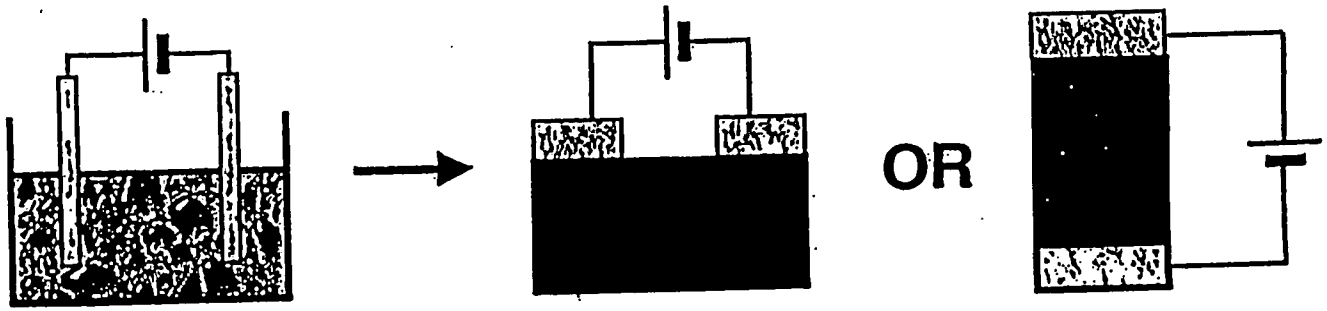
Solid Solutions

- Chalcogenides are compounds of S, Se, Te (and O)
  - As_2S_3, Ge_3Se_7, etc.
- Metals (e.g. Ag, Cu) can be dissolved in chalcogenide glass to form a solid solution
  - introduced by thermal diffusion or photodissolution (uv)
- Example - Ag in Ge_3Se_7
  - $Ge_3Se_7 = 3GeSe_2 + Se$ ($GeSe_2$ glass has SiO_2–like structure)
  - Ag reacts with excess Se (Ag_2Se) and acts as a network modifier - up to 32 at.% Ag possible
  - Ag in solution → Ag^+ and moves with field ($\mu = 10^{-5} - 10^{-4}$ $cm^2/V.s$?)
- Transport number is high
  - poor electronic conductors
  - solution resistivity is therefore high (hundreds of Ω.cm)

Electrochemistry

- **Solid solutions are not unlike liquid electrolytes!**



  - Cathode (conductor): $M^+ + e^- \rightarrow M$ *electrodeposition*
  - Anode (with excess M): $M \rightarrow M^+ + e^-$ *electrodissolution*

- **Redox reaction proceeds at low voltage**
  - approximately 0.18 V threshold
  - maintains M^+ concentration in solution
  - ions move through solution by a "coordinated motion"

confirmed through measurement. What things does it depend upon?

Which Material?

- We started with As_2S_3 and AsS_2 but ...
- Arsenic compounds pose technological challenges
  - toxicity
  - Ag precipitation
  - As outdiffusion and sublimation
  - low glass transition temperature

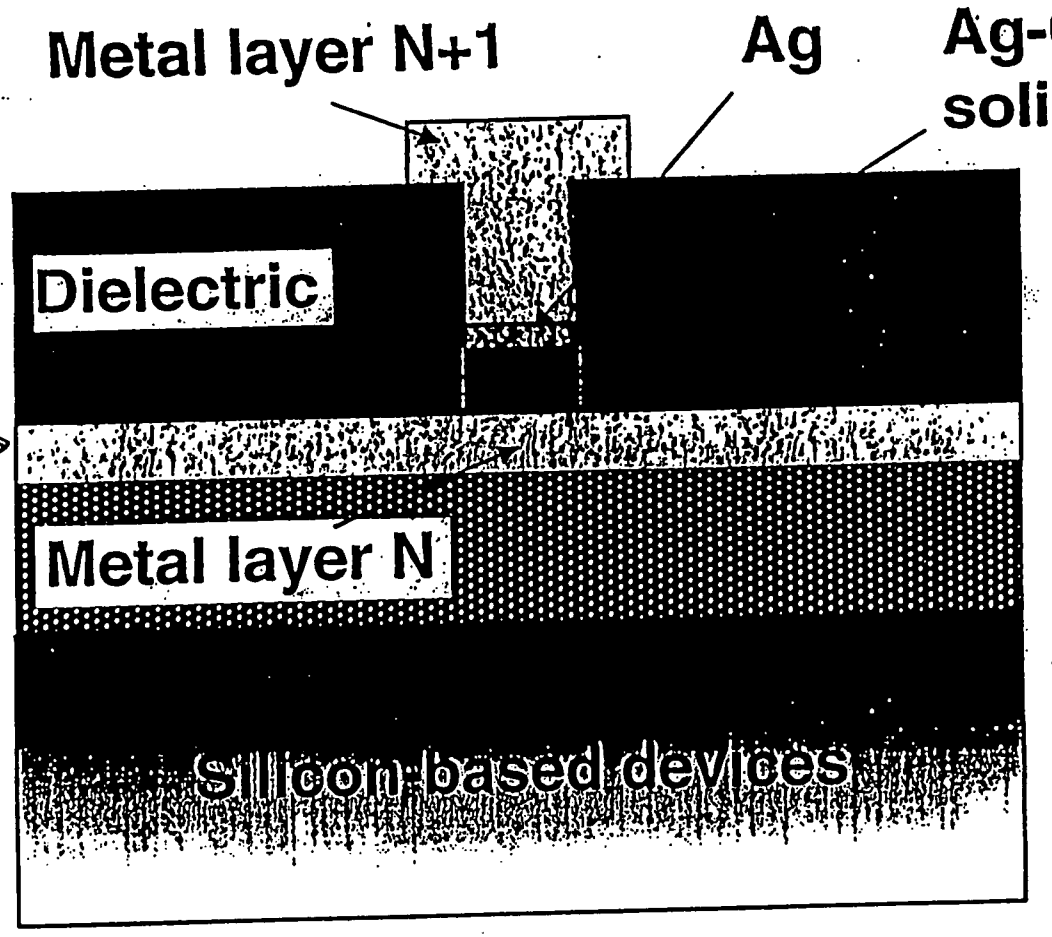
AsS_2 - 145ºC	As_2S_3 - 184ºC
$AsSe_2$ - 131ºC	As_2Se_3 - 173ºC

- Germanium compounds are better ...
  - better glass transition temperature

GeS_2 - 500ºC	Ge_3S_7 - 450ºC
$GeSe_2$ - 425ºC	Ge_3Se_7 - 400ºC

- On the other hand, tellurides stink!
  - weak bonding and unstable glasses
  - crystallizes very easily at low T (even at resist hard bake)
  - Te is very toxic

Example of an "Active in Via" Device



Top down:

< thickness 100Å

M1 →

Tried to use W, and it didn't work, we have to be concerned about reactors

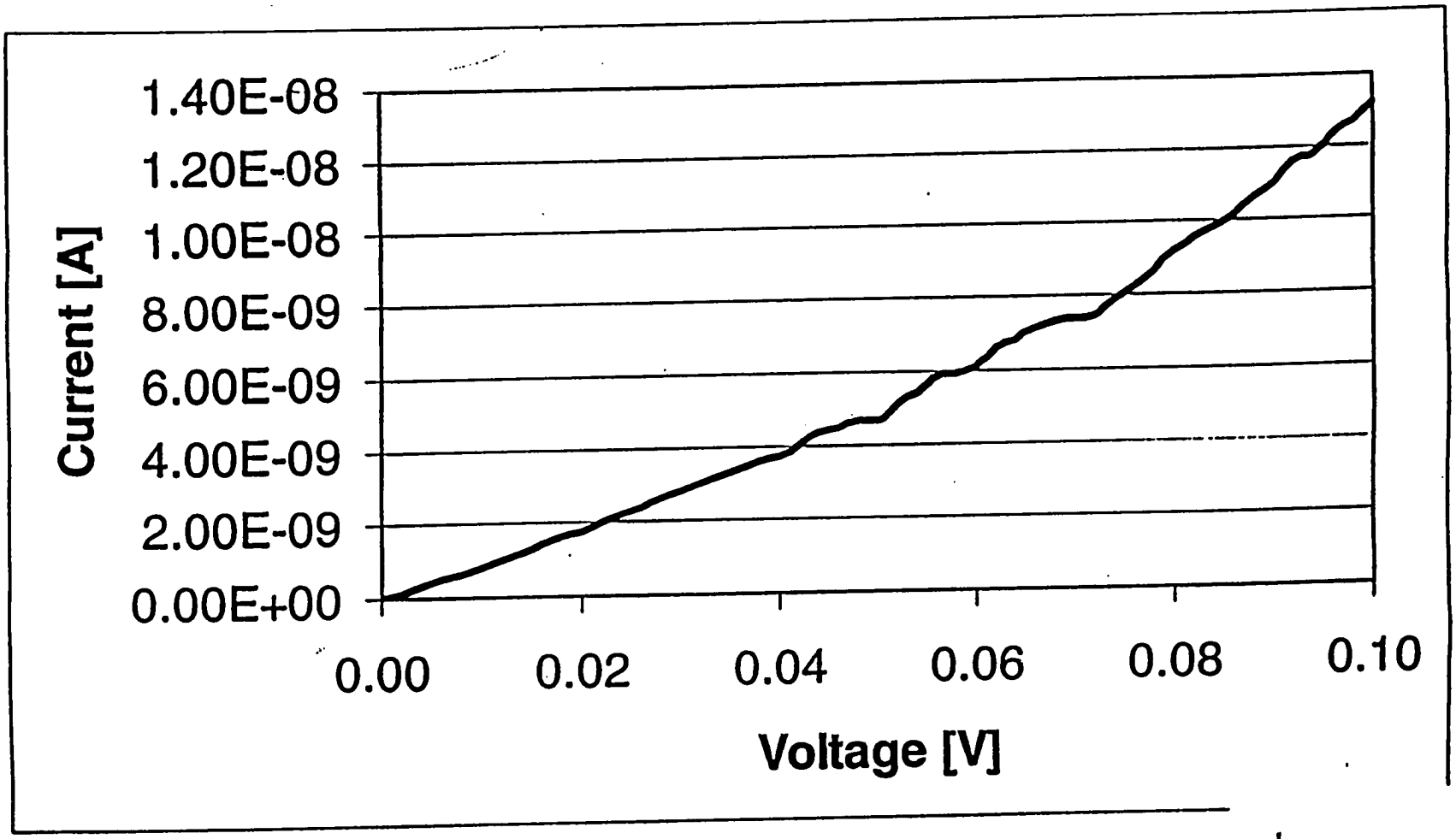
Ti, Cr, Mo, Ni, W work.
TiN also...

Ag as N+1...
E-migration is effect by field migration in the opposite direction

Electrical Characteristics: "Off State"

- **Solution resistance is high**
  - 100s $k\Omega.\mu m^2$ in a 30 nm long structure
- **Double layer at metal-solid solution interface leads to capacitive character**
  - capacitance in the order of 10 $fF/\mu m^2$
  - current flow is Schottky barrier-like, $I \sim e^{qV/kT}$
  - adds high small signal resistance (5 $M\Omega.\mu m^2$ @ 0.1V)
- **Additional tunneling barrier at cathode greatly increases resistance**
  - can increase overall resistance to tens of $G\Omega.\mu m^2$

Characteristics of 0.8 μm device with Ni cathode in off-state subthreshold region



Electrical Characteristics: "On State"

- Applied voltage above electrodeposition threshold results in growth of silver "wire" from cathode to anode
  - on surface of solution at interface with dielectric
- Electrodeposit growth shorts-out solution and double layer
  - greatly reduced resistance
  - purely metallic character
- Resistance of on state depends on amount of charge applied during electrodeposition

Charge Requirements

- **Sample calculation assumptions:**
  - Electrodeposition is 100% efficient - total charge required per cm^3 of Ag electrodeposit = 9.28×10^3 C
  - Electrodeposit has uniform cross section
  - Ag thin film resistivity is 100× the bulk value
- **For a 30 nm long connection with a resistance of 1 kΩ, electrodeposit volume is 1.35×10^{-18} cm^3.**
- **Charge required is 1.25×10^{-15} C**
- **Energy required is 0.25 fJ!** ← electrostatic discharge will switch the devices.
- **A constant applied current of 1 μA would allow switching in the nsec regime**
  - But high off resistance limits current!
  - What are the other limiting factors?
  - What about parasitics/double layer capacitance?

$= 1.417 \times 10^{-17}$ g Ag

$= 1.3186 \times 10^{-11}$ mol Ag

$= 79406$ atoms of Ag

Speed Predictions

- Growing electrodeposit becomes the cathode - high field at tip leads to preferential deposition
- Moving tip "harvests" ions from solution as it progresses and tip field increases
- Electrodeposit is typically very thin - around a nm thick (x 10s of nm wide) $(350\times10^{-8}\,c-)\times(100\times10^{-8}\,c-)\times(10\times10^{-8}\,c-) = 3.5\times10^{-19}$ $= 2.1\times10^{4}$ a
- Solution contains many tens at. % of metal and so it takes only a few nm of depth to supply growth
- Ions only have to move a few nm in high field
- If field is in the order of 10^6 V/cm and mobility is 10^{-4} $cm^2/V.s$, ion velocity will be 1 nm/nsec
- The ions therefore take only a few nsec to come out of solution

Self-Limiting On Resistance

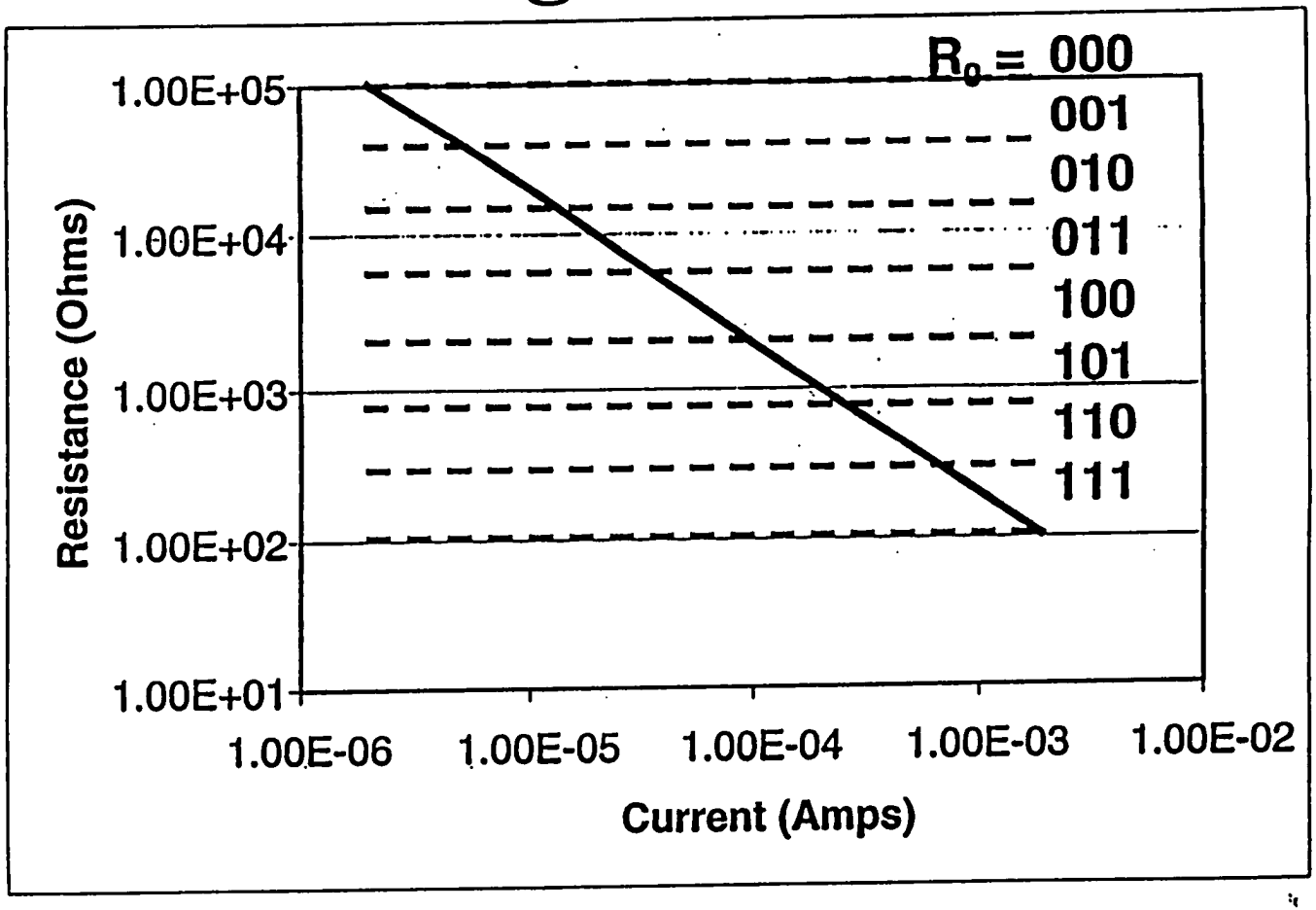
- If a constant current I_{const} is applied, the voltage across the device will depend on its resistance R by $V = I_{const}R$
- Electrodeposition will occur as long as the voltage is above the threshold (0.18 V)
- When the electrodeposit connection is formed, the resistance will drop and so will the voltage
- The final resistance R_{on} of the device is therefore determined by the expression

^ ogram with constant current ⇒ constant final resistance.

$$R_{on} = 0.18/I_{const}$$

- This leads to a programmable self-limiting on resistance

Multi-Bit Programming Scheme?



Range has been split into seven "bands", each ±45% (from each midpoint) wide

Importance of Asymmetry

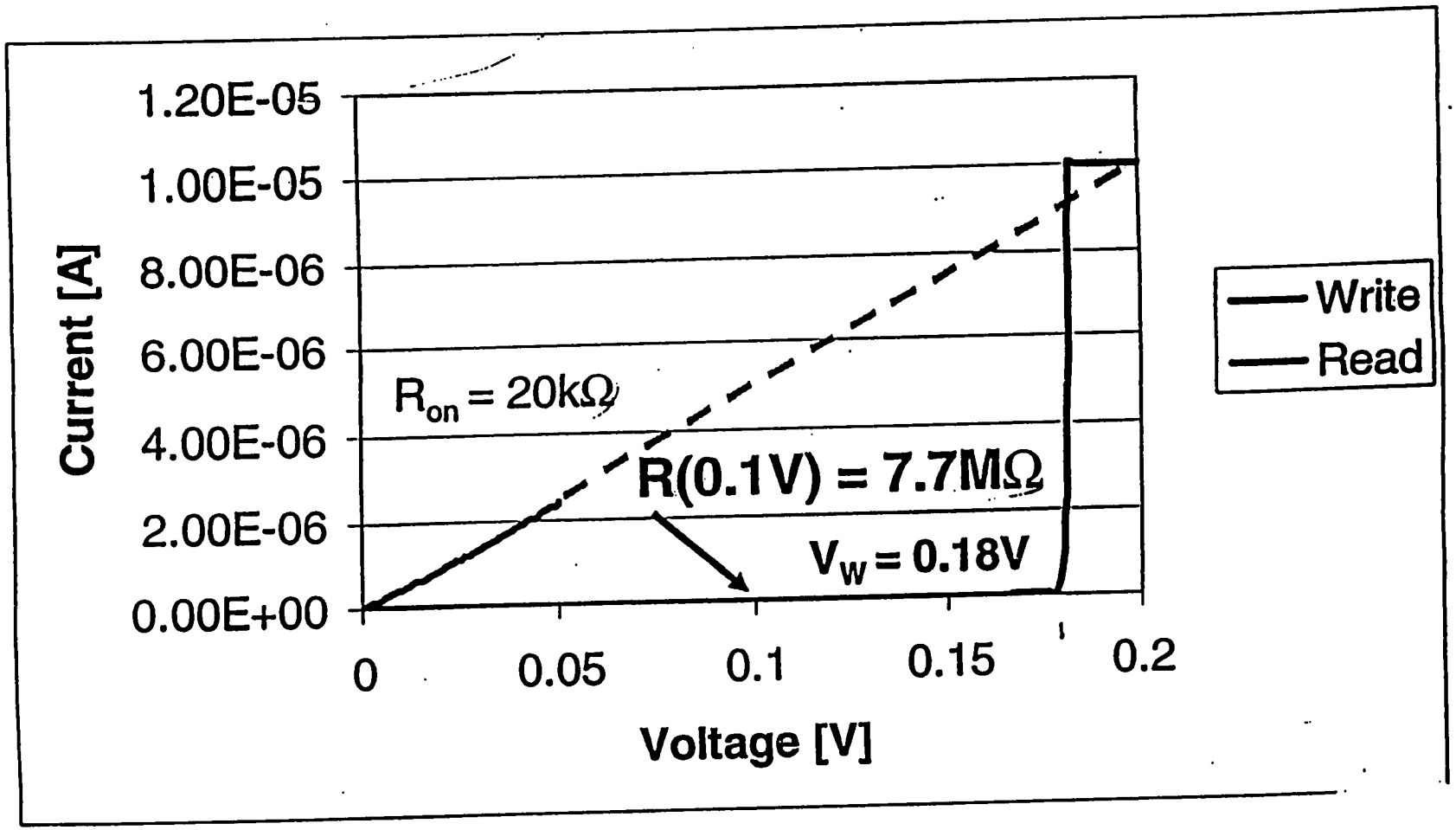
- Redox reaction will only proceed if the cathode can supply electrons and the anode can supply ions
- A device which has an "indifferent" cathode and excess metal at the anode can only form an electrodeposit in "forward bias"
- Once formed, electrodeposit is erased by applying a "reverse bias" above -0.18 V (−.20 volts)
  - redox reaction occurs in reverse
  - electrodeposit is now the anode and dissolves back into solution
  - electrodeposition occurs at the cathode (original anode) at the point where electrodissolution originally occurred

Control of Write Threshold

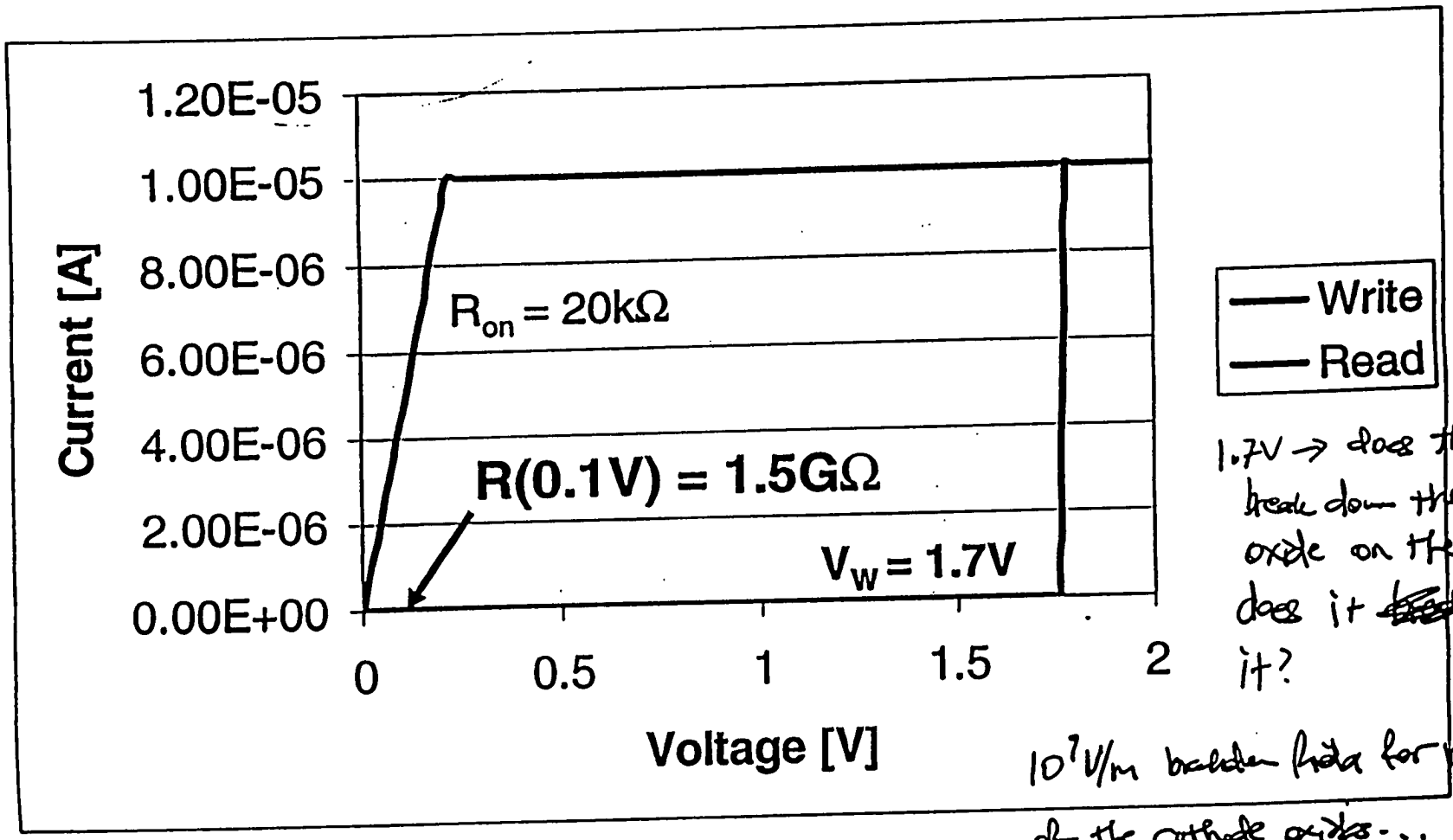
- Electrodeposition threshold is set by redox reaction - fundamental write/erase limit
- Write threshold may be significantly increased by placing a tunneling barrier on the cathode
- Electrodeposition occurs on this barrier as electrons can tunnel through to solution
- Connection from cathode to anode is not complete until barrier is broken down
- This occurs when applied voltage reaches V_b for the barrier - typically 1V/nm of thickness
- Barrier is "healed" during erase by anodic oxidation(?)

For Ni

Characteristics of 0.8 μm test device with low write voltage (V_W)



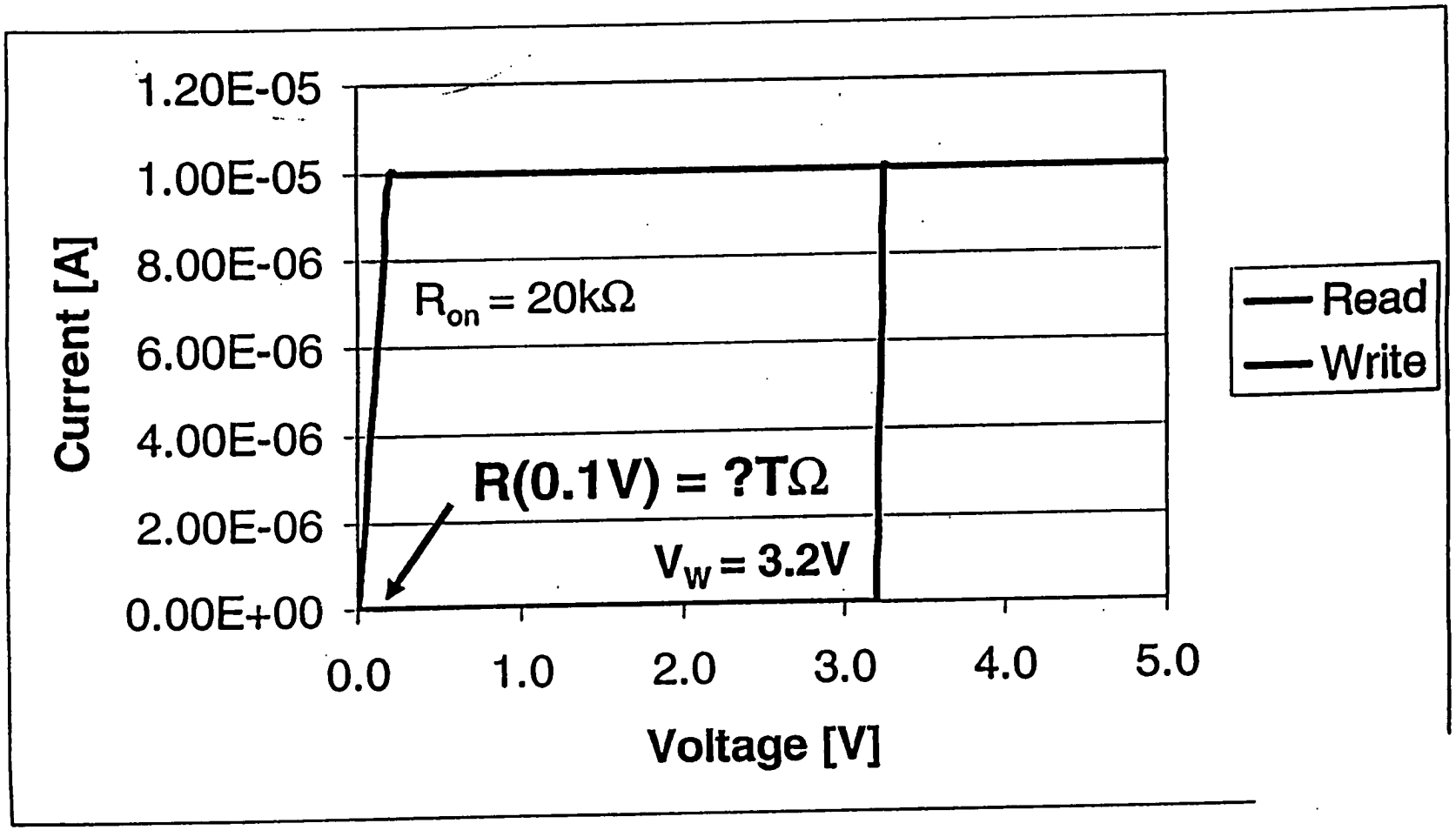
Characteristics of 4 μm test device with approximately 1.7 nm oxide on cathode



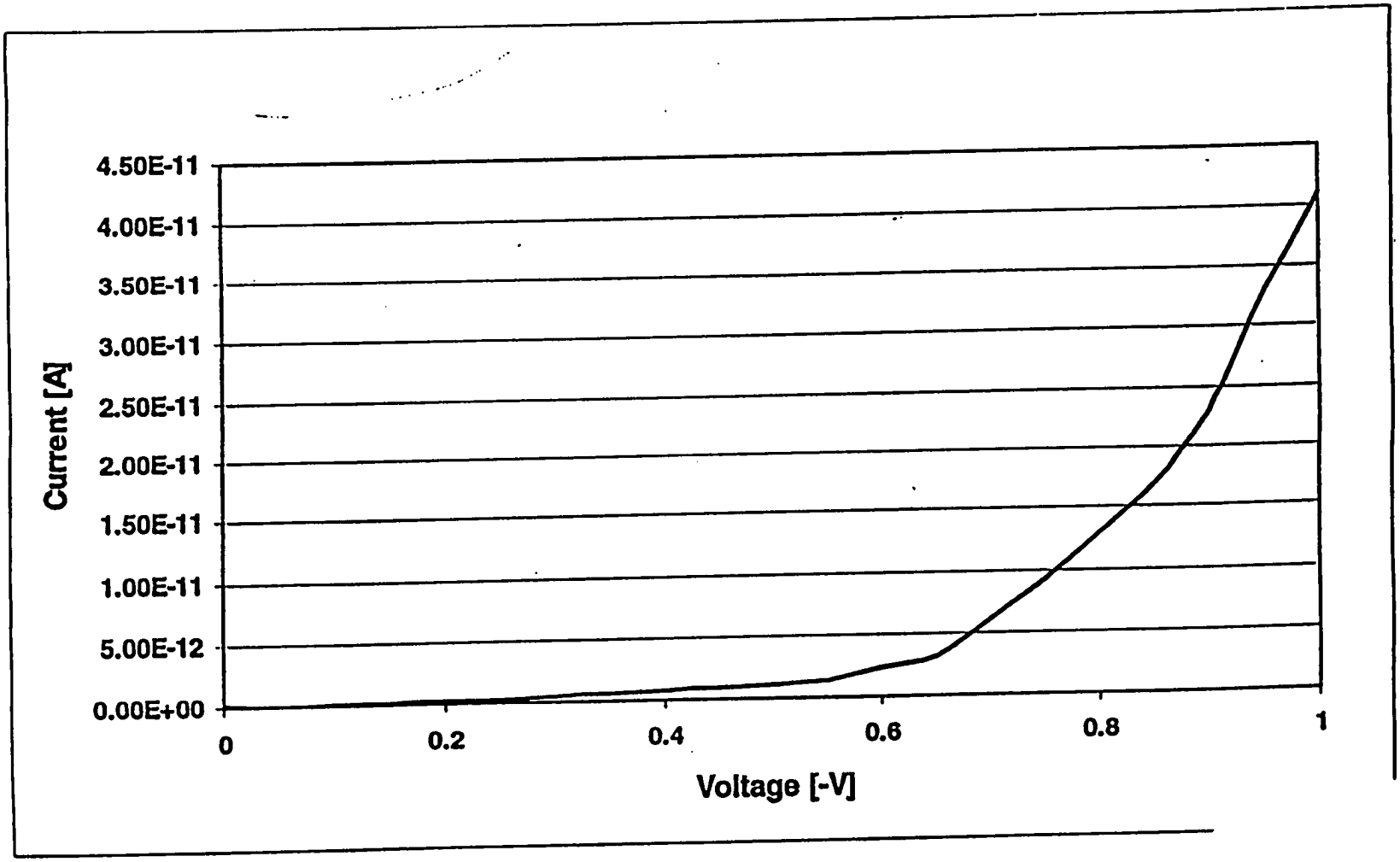
1.7V → does this breakdown the oxide on the N: ? does it ~~break~~ reduce it?

10^7 V/m breakdown fields for most of the cathode oxides...

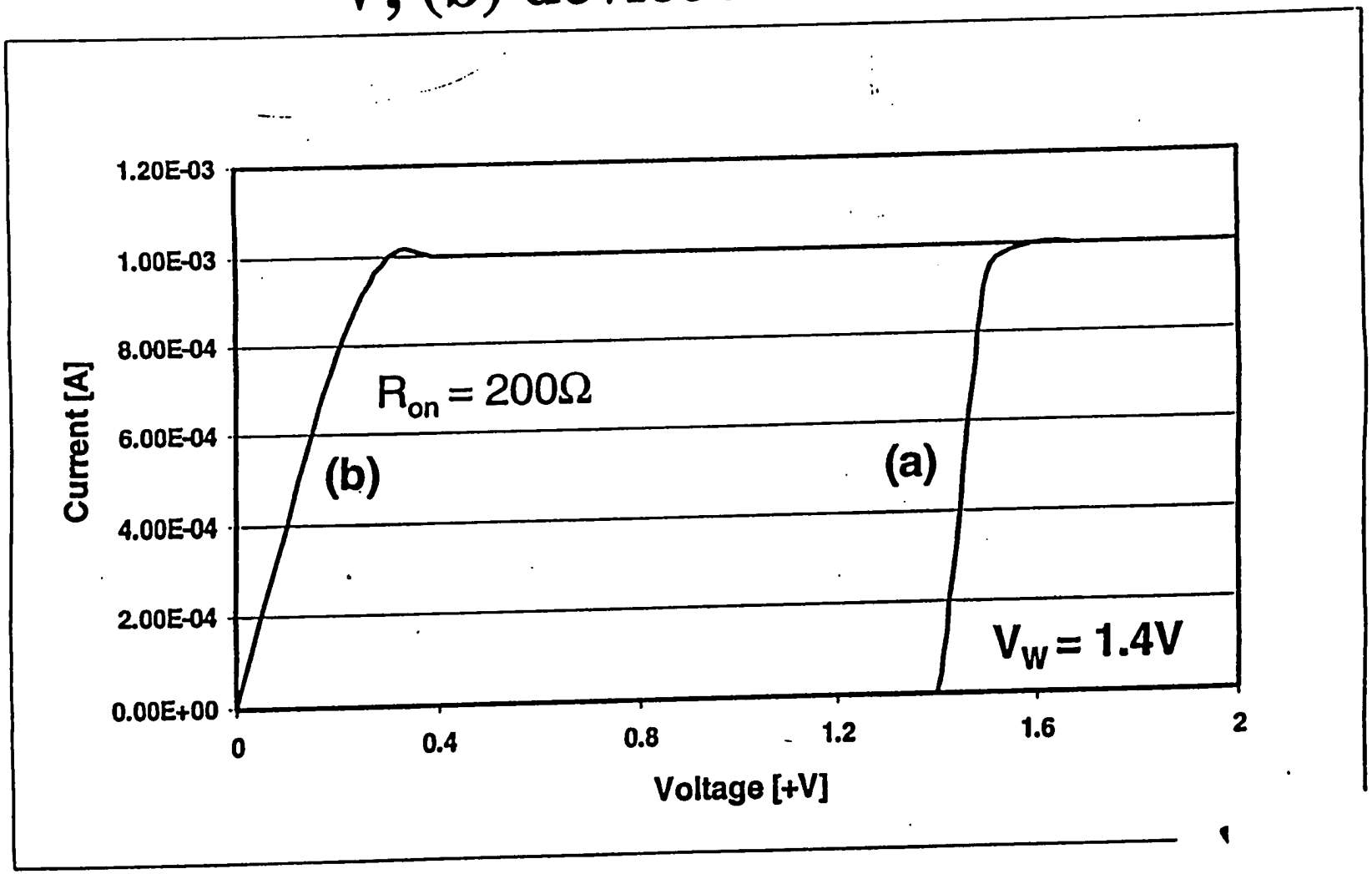
Characteristic of 4 μm test device with approximately 3 nm oxide on cathode



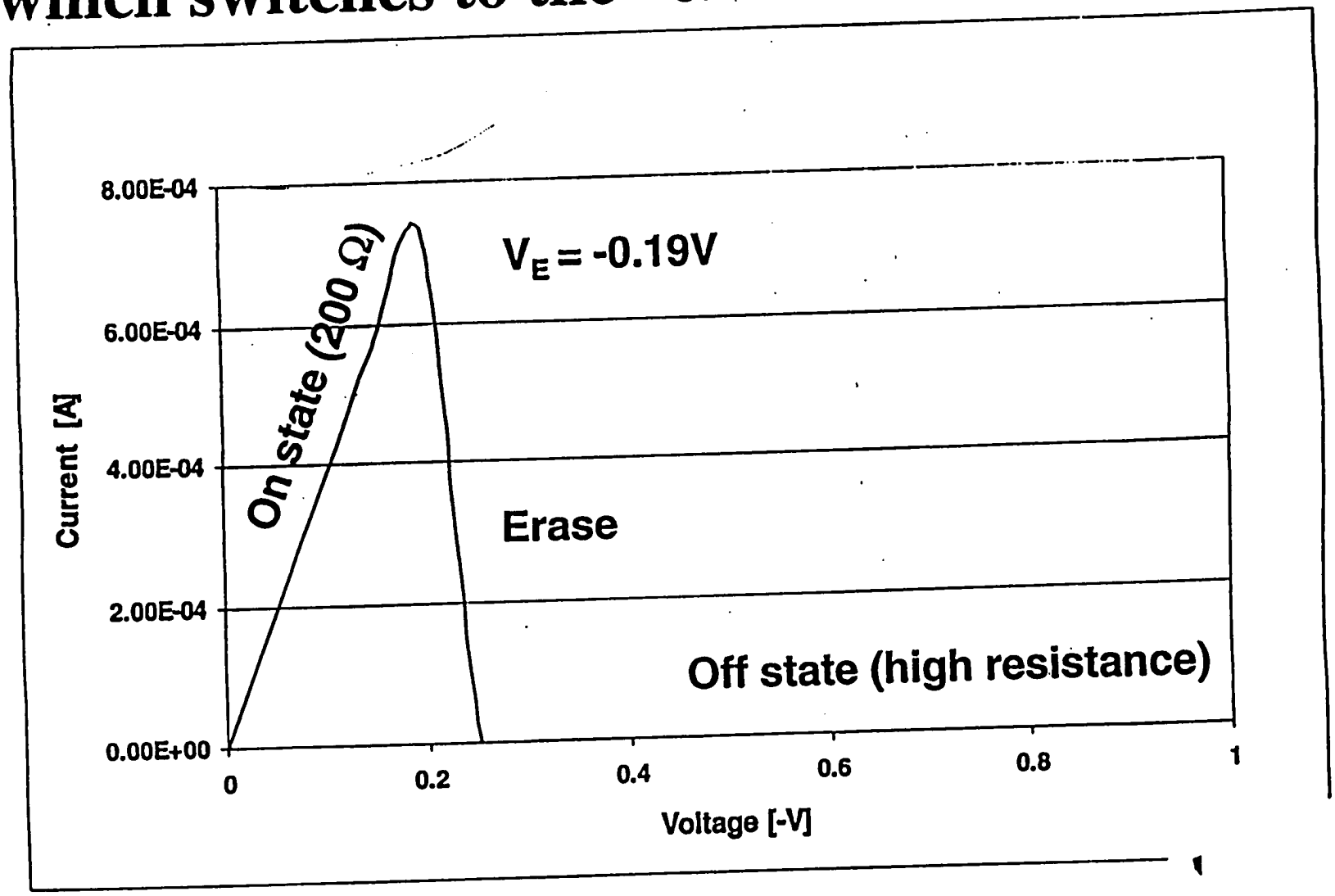
Characteristics of 4 μm device with approximately 1.4 nm native oxide on cathode in "off" state



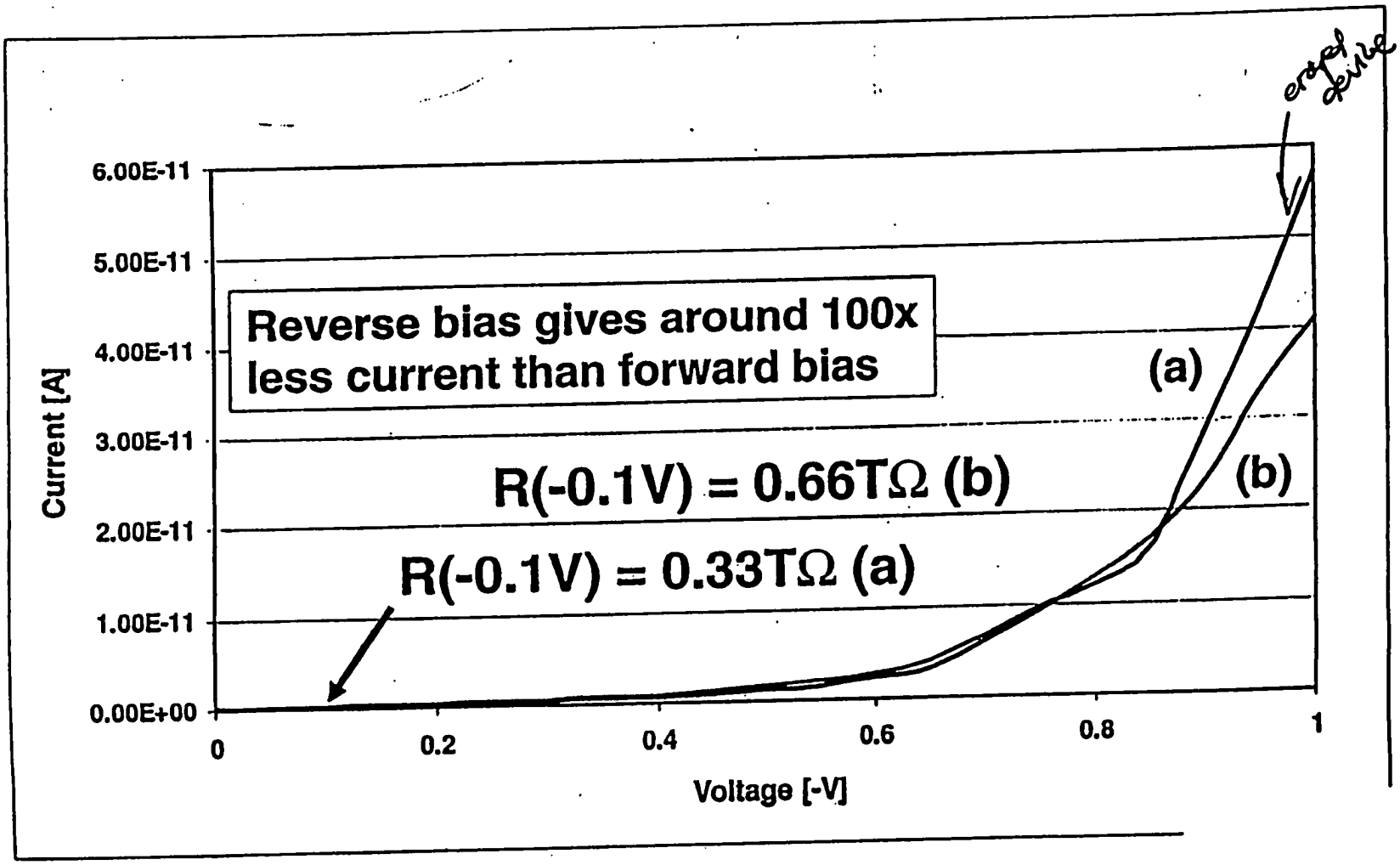
Characteristics of (a) device in the "off" state which switches to the "on" state at 1.4 V, (b) device in "on" state



Characteristics of device in the "on" state which switches to the "off" state around -0.2 V



Characteristics of (a) erased device compared with (b) unwritten device



Endurance and Retention

- Electrodeposition/electrodissolution cycle should be repeatable indefinitely in the absence of significant material changes
  - we have been able to demonstrate 10^7 to 10^8 cycles but
  - many devices fail in on-state after a few 1000 cycles
  - stuck bit is due to breakdown of surrounding dielectric
- Electrodeposit on "saturated" solid solution should be stable indefinitely
  - we have been able to show zero percent resistance change over several hours
  - measurement is affected by probe resistance changes
  - devices are highly sensitive and are susceptible to noise and discharge events

Read Strategies

- Devices are highly sensitive - presents problems for non-disturb read
- Possible read options are:
  - destructive - deliberately write or erase cell to detect state
  - low voltage (sub-threshold) - <0.18 V forward or reverse
  - short pulse (forward bias) to charge double layer only
    - » C_{dl} will be a fraction of a fF in a small geometry device
    - » A10 nsec pulse at 10 nA will charge this
    - » Charging current is "non-Faradaic" - no electrodeposition
- Non-destructive options essentially utilize current control or charge limiting

Issues

- **Materials deposition/device fabrication**
  - deposition methods
  - electrode materials
  - barrier materials
  - glass transition temperature
- **Thermal stability**
  - during processing
  - operation
- **Materials and device performance**
  - write, read, erase energy
  - retention, endurance
  - failure mechanisms
- **Etc.?!!**

Short Term Work at ASU

- **Build glass synthesis facility**
  - existing facility is inadequate
  - new facility will be in CSSER with controlled access
  - may use existing facility at U. Cincinnati to avoid delay
- **Synthesize source material for evaporation**
  - $GeSe_2$ as well as Ge rich and Se rich glasses
  - GeS_2 as well as Ge rich and S rich glasses
  - perform analysis
- **Fabricate basic test structures**
  - determine gross material properties
- **Continue to compile materials database**
  - information is sparse and scattered